AFRL-PR-WP-TR-2000-2007

FUEL STABILIZATION

MICHAEL M. COLEMAN
STEVEN P. FEARNLEY
SANAT KUMAR
MARIA SOBKOWIAK

PENNSYLVANIA STATE UNIVERSITY
110 TECHNOLOGY CENTER BLDG
UNIVERSITY PARK, PA 16802-7000

SEPTEMBER 1999

FINAL REPORT FOR 07/01/1995 – 12/31/1998

PROPULSION DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
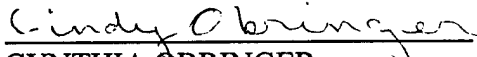WRIGHT-PATTERSON AIR FORCE BASE OH 45433-7251

20000211 096

NOTICE

USING GOVERNMENT DRAWINGS, SPECIFICATIONS, OR OTHER DATE INCLUDED IN THIS DOCUMENT FOR ANY OTHER PURPOSE OTHER THAN GOVERNMENT PROCUREMENT DOES NOT IN ANY WAY OBLIGATE THE US GOVERNMENT. THE FACT THAT THE GOVERNMENT FORMULATED OR SUPPLIED DRAWINGS, SPECIFICATIONS, OR OTHER DATA DOES NOT LICENSE THE HOLDER OR ANY OTHER PERSON OR CORPORATION; OR CONVEY ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL, ANY PATENTED INVENTION THAT MAY RELATE TO THEM.

THIS REPORT IS RELEASABLE TO THE NATIONAL TECHNICAL INFORMATION SERVICE (NTIS). AT NTIS, IT WILL BE AVAILABLE TO THE GENERAL PUBLIC, INCLUDING FOREIGN NATIONS.
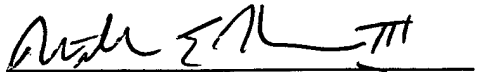
THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

CYNTHIA OBRINGER
Fuels Branch
Propulsion Sciences and Advanced Concepts Division

WILLIAM E. HARRISON III
Chief, Fuels Branch
Propulsion Sciences and Advanced Concepts Division

LEO S. HAROOTYAN
Deputy
Propulsion Sciences and Advanced Concepts Division

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE SEPTEMBER 1999	3. REPORT TYPE AND DATES COVERED FINAL REPORT FOR 07/01/1995 - 12/31/1998

4. TITLE AND SUBTITLE
FUEL STABILIZATION

5. FUNDING NUMBERS
C   F33615-98-D-2802
PE   62203
PR   3048
TA   05
WU   EX

6. AUTHOR(S)
MICHAEL M. COLEMAN, STEVEN P. FEARNLEY
SANAT KUMAR, MARIA SOBKOWIAK

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
PENNSYLVANIA STATE UNIVERSITY
110 TECHNOLOGY CENTER BLDG
UNIVERSITY PARK, PA 16802-7000

8. PERFORMING ORGANIZATION REPORT NUMBER

D.O. 001

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
PROPULSION DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AFB, OH 45433-7251
POC: CYNTHIA OBRINGER, AFRL/PRSF, 937-255-6390

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

AFRL-PR-WP-TR-2000-2007

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
The primary objectives of Delivery Order 0001 were threefold. The first was a fundamental study of high-temperature fuel stabilization performed to assess the practical temperature limits of hydrogen-donor stabilization. The second was an experimental study carried out to determine whether superior hydrogen-donor stabilizers could be designed and synthesized. The third was a study performed to determine the vulnerability of high-temperature hydrogen-donor stabilizers to oxidative degradation in the autoxidative temperature regime.

Delivery Order 0001 consisted of three tasks: Fundamentals of High-Temperature Stability, Design of Superior Stabilizers, and Low-Temperature Oxidation Resistance of Thermal Stabilizers. The results are presented in Sections 2.0, 3.0, and 4.0, respectively; Section 5.0 contains references.

14. SUBJECT TERMS
Fuel, Stability, High Temperature Fuels, Low Temperature Oxidation, Stabilizers

15. NUMBER OF PAGES
47

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

Table of Contents

List of Tables

List of Figures

1.0 INTRODUCTION

The primary objectives of Delivery Order 0001 were threefold. The first was a fundamental study of high-temperature fuel stabilization performed to assess the practical temperature limits of hydrogen-donor stabilization. The second was an experimental study carried out to determine whether superior hydrogen-donor stabilizers could be designed and synthesized. The third was a study performed to determine the vulnerability of high-temperature hydrogen-donor stabilizers to oxidative degradation in the autoxidative temperature regime.

Delivery Order 0001 consisted of three tasks: Fundamentals of High-Temperature Stability, Design of Superior Stabilizers, and Low-Temperature Oxidation Resistance of Thermal Stabilizers. The results are presented in Sections 2.0, 3.0, and 4.0, respectively; Section 5.0 contains references.

2.0 FUNDAMENTALS OF HIGH-TEMPERATURE STABILITY

2.1 Background

During the past few years hydrogen donors such as tetrahydroquinoline (THQ), tetralin (THN), and benzyl alcohol (BzOH) have been investigated as potential high-temperature stabilizers for jet fuels in the pyrolytic regime (> 400 °C) [1-4]. While the results have been most promising, kinetic studies have revealed [4] that the rate of hydrocarbon decomposition is a very strong function of temperature in the range from 400 to 500 °C. This is nicely illustrated in Figure 2.1. The top graph shows the amount of dodecane (Dod) remaining in mixtures, which initially contained 10-mol % THQ, as a function of stressing time for temperatures of 400, 425, and 450 °C. The initial concentration of Dod is denoted by c_{A_0}, and the amount remaining after a particular time of thermal stressing at a given temperature by c_A. The bottom graph shows the amount of THQ remaining in the mixture. The striking temperature dependence implies that

adequate stabilization of hydrocarbon fuels using hydrogen donors at temperatures much above 500 °C will be extremely difficult, if not impossible [4].

During the time period of this delivery order, kinetic data for a THN/tetradecane (TD) system was compiled in order to develop appropriate models for pyrolytic flow reactor behavior [4,5].

Thermal stressing was performed on mixtures of 10-mL TD and 0.523-mL THN (equivalent to 10 mol%) in stainless-steel tubing bombs. After an initial purging with UHP-grade N_2 (1000 psi, five times), reactors were pressurized to 100 psi N_2 and heated at 400, 425, or 450 °C for the required period of time, prior to quenching and opening. The resulting mixtures were analysed by GC-MS. The amount of TD remaining was assessed by comparison of its peak area with that for the total degradation products, and normalized with respect to values obtained for an external standard of the initial starting mixture. Appropriate plots are shown in Figures 2.2 and 2.3.

From the slopes of the straight lines the following rate-constant values were obtained: $k_{400°C} = 2.25 \times 10^{-6}$; $k_{425°C} = 2.89 \times 10^{-5}$, and $k_{450°C} = 1.08 \times 10^{-4}$ s^{-1}. An apparent activation energy (E_a) of 75.2 kcal mol^{-1} was determined from an Arrhenius plot of ln k vs T^{-1} (Figure 2.3).

This is commensurate with values previously obtained for similar systems:

pure dodecane	58 kcal mol^{-1}	⎫
dodecane/BzOH	67 kcal mol^{-1}	⎬ [4]
dodecane/THQ	71 kcal mol^{-1}	⎭
pure tetradecane	68 kcal mol^{-1}	[6]
tetradecane/THN	75 kcal mol^{-1}	*this work*

To summarize, at relatively low temperatures in the pyrolytic regime (about 425 °C), the degradation of jet fuel proceeds through a chain reaction with the formation of

free radicals. If we can "kill" these free radicals, especially at the point of inception, we can, in principle, inhibit the degradation of jet fuels. This, of course, is the function of the hydrogen donor. However, at relatively high temperatures (> 500 °C) spontaneous cleavage of C–H and C–C bonds is facile in both the hydrocarbon and the organic hydrogen-donor stabilizer. In other words, there is clearly a temperature above which the rate of hydrocarbon bond cleavage completely overwhelms the rate of hydrogen transfer from a potential hydrogen donor (which itself is subject to bond cleavage at this temperature), and this implies that the degradation of the jet fuel will proceed rapidly to the formation of carbonaceous solids. The question addressed here is the following, "Can we estimate the highest temperature attainable for hydrogen-donor stabilized jet fuels?"

2.2 A Simple Model

Consider the following very simple model [8]. To describe the time dependence of the fuel degradation the following reactions were considered using dodecane (Dod) as a representative linear chain-like hydrocarbon that is a typical major component of jet fuels. A hydrocarbon molecule such as Dod, in the absence of molecular oxygen and stabilizers, can break either spontaneously (eq. 1) or after collision with a primary free radical $R^{\bullet}$ (eq. 2).

$$Dod \xrightarrow{k_1} 2R^{\bullet} \tag{1}$$

$$Dod + R^{\bullet} \xrightarrow{k_2} Dod^{\bullet} + RH \tag{2}$$
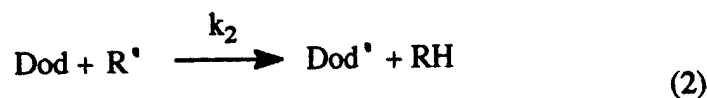
Chain cleavage of the $Dod^{\bullet}$ radical results in the formation of a terminal alkene and primary radical:

$$Dod^{\bullet} \xrightarrow{k_3} R^{\bullet} + CH_2=CH-CH_2\text{wwwww} \tag{3}$$
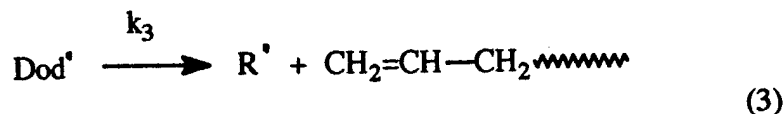
Abstraction of hydrogen from the methylene group allylic to the vinyl end group is facile leading to rapid degradation of molecular weight and the formation of conjugated species, which are thought to be precursors to carbonaceous solids. In the presence of a thermal stabilizer (hydrogen donor), which is denoted SH_n, the stabilizer suppresses these reactions by donating hydrogen atoms:

$$Dod^{\bullet} + SH_n \longrightarrow Dod + SH_{n-1}^{\bullet}$$

$$Dod^{\bullet} + SH_{n-1}^{\bullet} \longrightarrow Dod + SH_{n-2}$$

$$Dod^{\bullet} + SH_{n-2} \longrightarrow Dod + SH_{n-3}^{\bullet}$$

$$Dod^{\bullet} + SH^{\bullet} \longrightarrow Dod + S$$

$$(4)$$

and:

$$R^{\bullet} + SH_n \longrightarrow RH + SH_{n-1}^{\bullet}$$

$$R^{\bullet} + SH_{n-1}^{\bullet} \longrightarrow RH + SH_{n-2}$$

$$R^{\bullet} + SH_{n-2} \longrightarrow RH + SH_{n-3}^{\bullet}$$

$$R^{\bullet} + SH^{\bullet} \longrightarrow RH + S$$
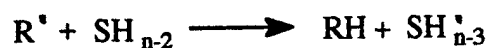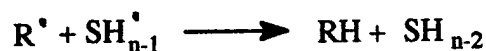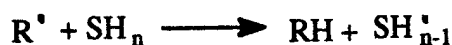
$$(5)$$

For BzOH, $n=2$, and for THQ or THN, $n=4$.

The relevant parameters in this system are the concentrations of Dod, SH_n, and their corresponding radicals. It is assumed that all reactions in eqs. (4) and (5) except the initial ones are very fast. Therefore, in the steady-state approximation [7] the kinetics of the process is determined by the rate of the first reactions only. Also assumed is that the

first reactions in eqs. (4) and (5) have the same rates k_4. Then the kinetic equations for the system have the following form:

$$\frac{d[Dod]}{dt} = -k_1[Dod] - k_2[Dod][R^\bullet] + nk_4[Dod^\bullet][SH_n] \qquad (6)$$

$$\frac{d[Dod^\bullet]}{dt} = k_2[Dod][R^\bullet] - k_3[Dod^\bullet] - nk_4[Dod^\bullet][SH_n] \qquad (7)$$

$$\frac{d[R^\bullet]}{dt} = 2k_1[Dod] - k_2[Dod][R^\bullet] + k_3[Dod^\bullet] - nk_4[R^\bullet][SH_n] \qquad (8)$$

$$\frac{d[SH_n]}{dt} = -k_4[Dod^\bullet][SH_n] - k_4[R^\bullet][SH_n] \qquad (9)$$

In the steady state approximation [7] we can write down:

$$\frac{d[Dod^\bullet]}{dt} = \frac{d[R^\bullet]}{dt} = 0 \qquad (10)$$

which leads to:

$$\frac{d[Dod]}{dt} = -k_1[Dod] - \frac{2k_1k_2k_3[Dod]^2}{nk_4[SH_n]\left(nk_4[SH_n] + k_3 + k_2[Dod]\right)} \qquad (11)$$

$$\frac{d[SH_n]}{dt} = \frac{2k_1}{n}[Dod] \qquad (12)$$

Dividing eq. (12) by eq. (11), we obtain:

$$\frac{d[SH_n]}{d[Dod]} = \frac{2}{n}\left[1 + \frac{2k_2k_3[Dod]}{nk_4[SH_n]\left(nk_4[SH_n] + k_3 + k_2[Dod]\right)}\right]^{-1} \qquad (13)$$

For successful stabilization, the second term in eq. (6) should be small with respect to the first one. In other words, the second term in brackets in eq. (13) is small. If we neglect it, we can easily solve this equation obtaining:

$$[SH_n] = \frac{2}{n}\left([Dod] - D_0\right) + S_0 \qquad (14)$$

9

where D_0 and S_0 are the initial concentrations of Dod and stabilizer, respectively. This equation shows that stabilizer concentration depends upon the Dod concentration in a linear fashion.

If the initial concentration of stabilizer is large enough ($S_0 \gg 2 D_0 /n$), then it is enough stabilizer to sustain this regime. However, this is not the case for practical applications. Usually the initial concentration of stabilizer is relatively small ($S_0 / D_0 \leq 0.1$). This means that at some point $[SH_n]$ becomes very low, and the second term in eq. (6) is no longer negligible. We will call this event stabilization failure.

Accordingly, the time evolution of Dod concentration consists of two different regimes:

(1) The Stabilized Regime. In this regime the stabilizer snares all the free radicals formed and the only cause of fuel degradation is the cleavage of carbon-carbon bonds leading to a reduction of the overall molecular weight. The time dependence of the Dod for this regime is:

$$[Dod] = D_0 \exp(-k_1 t) \tag{15}$$

Even in this case it is important to note that the concentration of Dod decreases exponentially with time. The exponential dependence is controlled by a rate constant, k_1, which itself is a temperature-dependent quantity. Since this may reasonably be described by an Arrhenius dependence, with an activation energy of approximately 10 kcal/mole, this constant doubles with a 20°-C change in temperature. Accordingly, even in the stabilized region the fuel will degrade rapidly with increasing temperature.

(2) The Destabilized Regime. In this regime there is not enough stabilizer to catch all free radicals, and fuel rapidly degrades. In this case the fuel is degraded not only by the cleavage of the Dod, but also by additional reactions of the free radicals with the Dod. This is autocatalytic, with rate constants that increase exponentially with

10

temperature. Consequently, in this limit the fuel will degrade, virtually instantaneously [i.e. in a time frame of seconds].

To obtain the duration of the stabilized regime we need to solve eqs. (6) and (9). However, for a rough estimate we can use eq. (14). It follows from this equation that at the end of this regime the concentration of Dod is given by:

$$\frac{[\text{Dod}]_m}{D_0} \approx 1 - \frac{n}{2}\frac{S_0}{D_0} \tag{16}$$

Assuming that $S_0 / D_0 \approx 0.1$ and $n = 4$, this regime lasts until about 20% of Dod degrades. Both of these assumptions—that about 20% of Dod has degraded during the stability regime and that the amount of stabilizer in this regime varies with the amount of Dod in a linear fashion—are corroborated by the experimental data (Figure 2.1). From eq. (15), it follows that the duration of the stabilized regime is given by

$$t = -\tau \ln\left(1 - \frac{n}{2}\frac{S_0}{D_0}\right) \tag{17}$$

where τ is the characteristic time for cleavage of Dod.

In order to estimate the rate constants for these reactions, which will also permit quantitative estimates of the lifetimes of Dod, attempts were made to fit the rate equations to experimental data on the kinetics of degradation. While we can obtain order-of-magnitude estimates for these quantities, we encountered serious problems in the quantitative estimation as the set of equations to be solved (to obtain the rate constants) is very stiff. This arises because for each rate constant, we need to obtain the prefactor and the activation energy to describe its Arrhenius dependence. Since the rate constants change dramatically with temperature, the rate equations are very stiff and not amenable to solution. This is an unsolved problem at this time, one that needs to be addressed in the future.

11

2.3 Ramifications

To summarize, the degradation of Dod becomes faster, exponentially, with increasing temperature. Qualitatively, we can argue that the time required for degradation will decrease by a factor of 2 for every 20°-C increase in temperature. This means that over a 200°-C range, Dod will degrade 1000 times faster! Thus, although a jet fuel can be stabilized fairly readily at 300-400° C, it appears unlikely that fuels at temperatures much greater than 475° C can be stabilized. This conclusion is of course applicable only to a regime where an excess of the free-radical scavengers exists, and there is no reaction between free radicals and Dod.
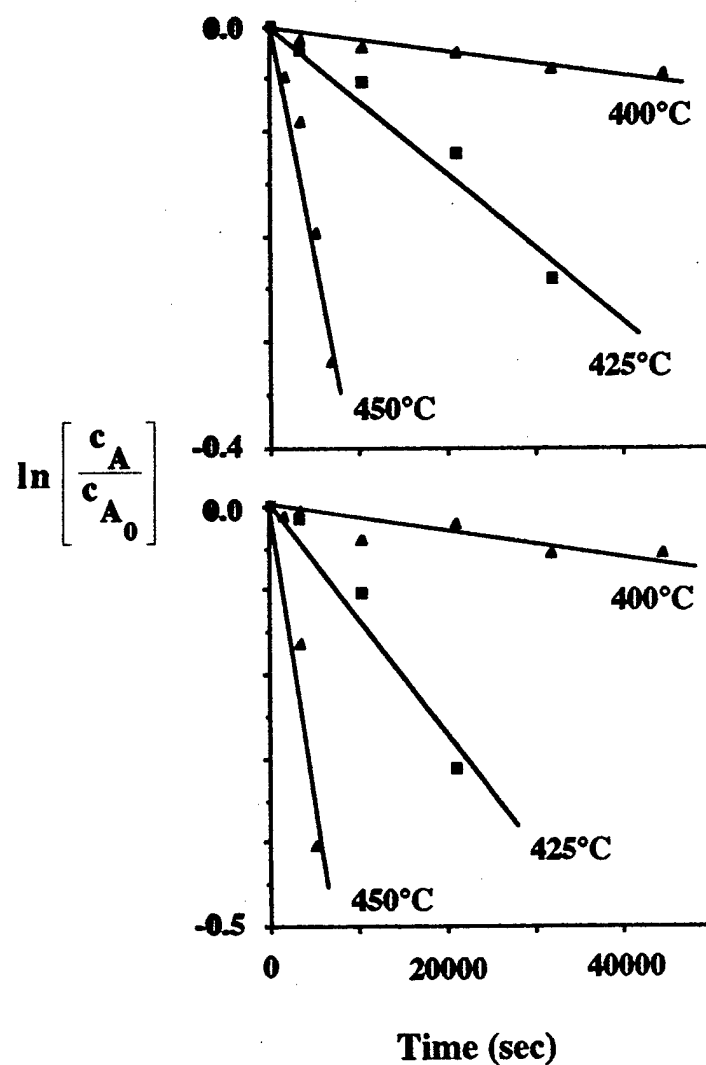
Figure 2.1. Plot of ln [c_A / c_{A_0}] versus time for Dod (top) and THQ (bottom) for a Dod mixture containing 10-mol % THQ at temperatures of 400, 425, and 450 °C.
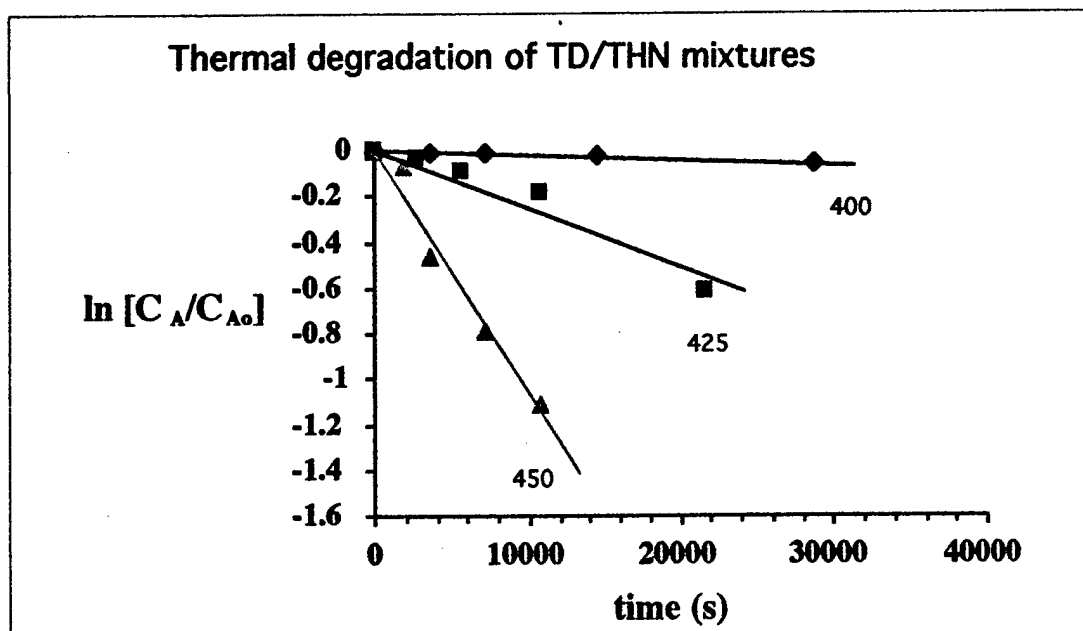
Figure 2.2. Plot of ln [c_A / c_{A_0}] versus time for TD/THN mixtures containing 10-mol % THN at temperatures of 400, 425, and 450 °C.
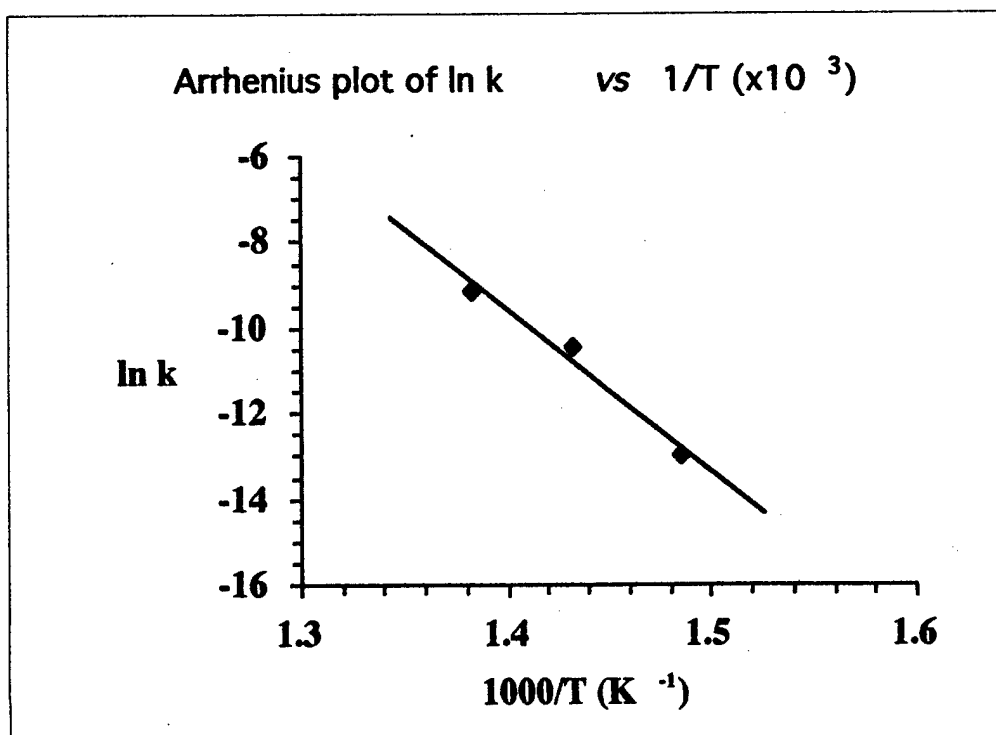
Figure 2.3. Plot of ln k versus T^{-1} for TD/THN mixtures.

3.0 DESIGN OF SUPERIOR STABILIZERS

3.1 Background

In recent years a number of novel hydrogen-donor molecules have been identified as potential high-temperature thermal stabilizers for jet fuels [1-3]. Three in particular have proved effective in model studies at elevated temperatures (400-480°C; 750-900°F): tetrahydroquinoline (THQ), tetrahydronaphthalene (THN), and benzyl alcohol (BzOH).
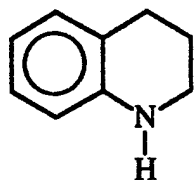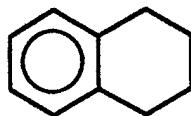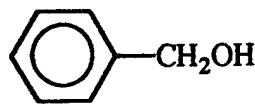
Examination of the thermolysis products has confirmed that all three operate by donation of multiple hydrogen atoms to quench the radical species responsible for fuel degradation. However, it should be noted that while the reactivity or efficiency of the hydrogen donors in the pyrolytic regime (> 400° C) decreases in the order THQ > THN > BzOH, so unfortunately does their susceptibility to autoxidation at lower temperatures (see Section 4.0). THQ and tetralin each donates four hydrogens with the formation of stable aromatic compounds (quinoline and naphthalene, respectively) as the ultimate driving force. The mechanism of BzOH stabilization is somewhat more obscure, involving an analogous stepwise loss of two hydrogens that results in a formal oxidation to benzaldehyde. Further oxidation, disproportionation, combination, etc., of this intermediate product may all play an important role.

This contrasting efficiency over a range of temperatures led to a consideration of the following questions: (1) What if the crucial structural elements neccessary for stabilisation in both the autoxidative and pyrolytic regimes were combined within the

same molecule? (2) Would complementary antioxidant abilities allow access to the full range of stabilization? (3) Would synergistic effects now come into play, whereby enhanced capabilities were observed? (4) What are the effects of substitution pattern? (5) Finally, how would all this differ from direct use of admixtures?

3.2   Hybrid Stabilizers

With these questions in mind, a series of studies aimed at the development of novel "hybrid" stabilizers based on a combination of two or more of our existing candidate additives was undertaken [9]. For example, "crossing" BzOH with THN leads to three new compounds shown schematically below, each containing the necessary features of their "parents", i.e. a benzylic alcohol moiety and a partially reduced naphthalene. Indeed, some precedent for this approach already exists within our own prior studies, as we have previously shown that 1,2,3,4-tetrahydro-1-naphthol (THNL) proves marginally more effective in the prevention of Dod degradation at high temperatures (450 °C under 1 MPa of N_2).
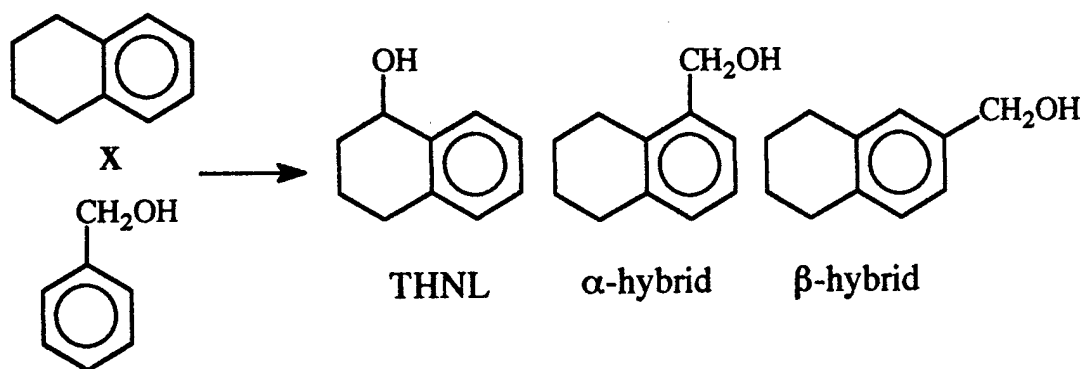
However, unlike THNL, which is commercially available, provision of the other hybrids in the quantities necessary for preliminary degradation studies required an expedient synthetic route. A thorough examination of the literature [10] revealed both hybrids to be known compounds, though no direct synthesis was available. Reduction of

the corresponding carbonyl compounds suggested itself as a viable alternative. The initial direct approach utilized a modified Friedel-Crafts type formulation of THNL itself [11], yielding a mixture of both α- and β-aldehydes, Scheme 3.1. Ensuing sodium borohydride reduction [12] was carried out under slightly acidic conditions to preclude competing acetal formation. Despite careful distillation (110-120°C @ 300-400 milliTorr), the isomeric alcohols proved inseparable and were isolated as a 1:1.7 mixture of the α and β isomers (denoted α,β-mix) in 64% yield over the two steps.

1.7:1 β - α
64% over 2 steps
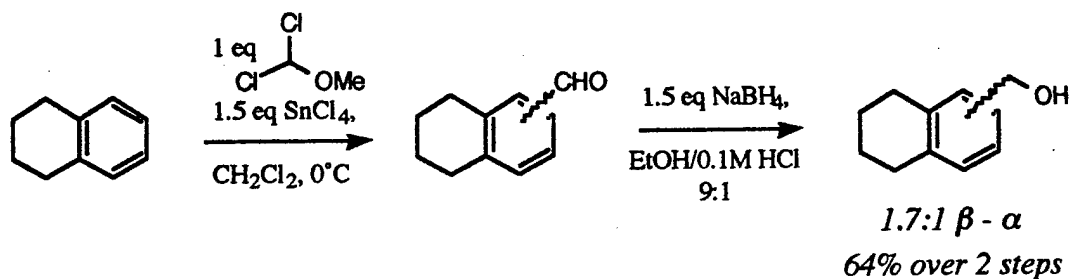
Scheme 3.1

Although this readily available mixture appeared attractive for the purpose of long-term studies, the pure α- and β-hybrids were required in order to investigate the effect, if any, of substitution pattern. Thus a regiospecific route was sought. In the case of the α-hybrid, the corresponding bromide had been reported with remarkable and exclusive regioselectivity [13]. An ensuing carbonylation, either of the Grignard-type or palladium mediated, would yield the necessary substrates for reduction. However, investigation of this alternative revealed the initial bromination to be entirely non-regiospecific, contrary to initial claims.

One answer to this question of regioselectivity was to start with the commercially available reduced α-naphthol and proceed *via* its triflate [14], similar in reactivity to the corresponding halide, Scheme 3.2. A standard triflation [15], followed by palladium-

mediated carbonylation [16], yielded the α-ester in excellent yield. Simple lithium aluminum hydride reduction afforded the required benzylic alcohol.

OH → 1 eq Tf₂O, 1 eq NEt₃, CH₂Cl₂, 0°C to rt → OTf 94% → CO (40 psi), 3% Pd(OAc)₂, 3% dppp, 2.2 eq NEt₃ / DMSO/MeOH 3:2, 70°C, 24 h

CO₂Me 97% → 1 eq LiAlH₄ / THF, 0°C to rt → OH quant
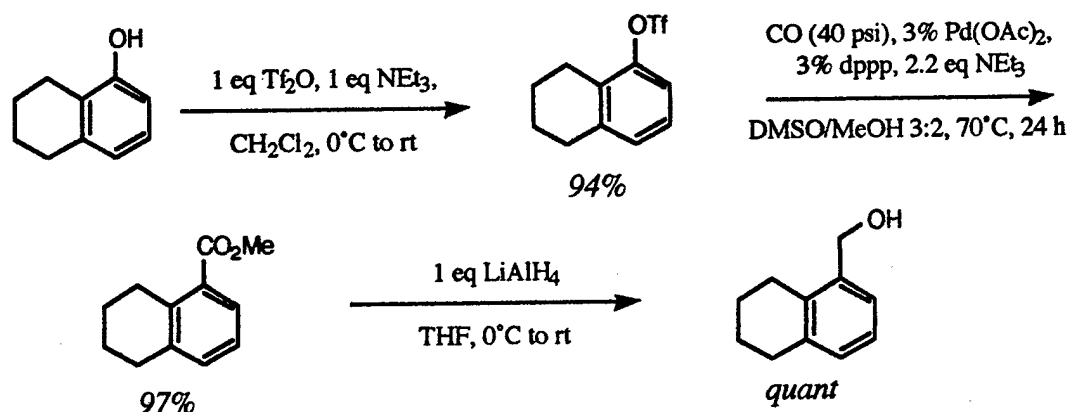
Scheme 3.2

An identical strategy was adopted for the β-hybrid, Scheme 3.3. An initial triflation proceeded uneventfully. However, whereas the use of moderate pressures (about 40 psi CO) in a sealed apparatus (Parr high-pressure reactor) had afforded the α-ester in near quantitative yield, application of this methodology to synthesize the β-hybrid under otherwise identical conditions gave a significantly lower yield (40%).

OH → 1 eq Tf₂O, 1 eq NEt₃, CH₂Cl₂, 0°C to rt → OTf 94% → CO (40 psi), 6% Pd(OAc)₂, 6% dppp, 2.2 eq NEt₃ / DMSO/MeOH 3:2, 70°C, 3 d

CO₂Me quant → LiAlH₄ / THF, 0°C → OH 55%
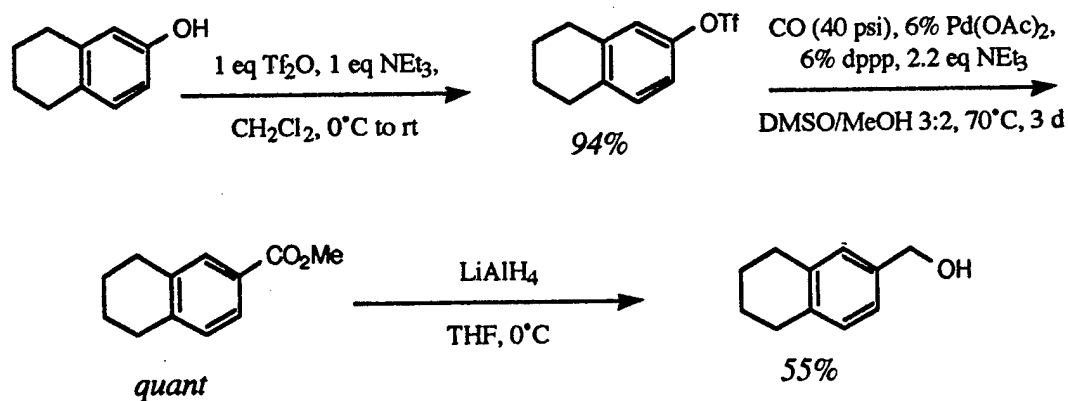
Scheme 3.3

One possible explanation for this apparent difference in reactivity can be invoked upon consideration of the catalytic pathways involved. As can be seen in the α-case, equilibration from an initial Pd (II) complex to the acyl palladium species is driven by the release of considerable peri-type steric strain; in the β-case no such enhancement mechanism exists, leading to the overall slower rate of ester formation:
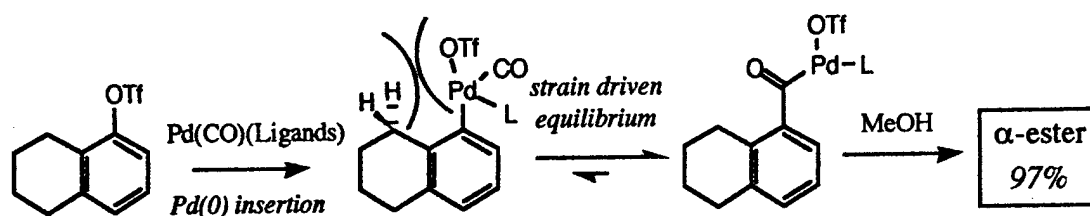
Fortunately a simple doubling of the initial catalyst loading (6%) and increased reaction time (3 days) afforded the intermediate ester quantitatively. Ensuing hydride reduction furnished the required alcohol (albeit in somewhat lower isolated yield due to some accidental sample loss.)

Simple thermal-stressing studies of these novel second-generation BzOH-THN hybrids were performed, using the now familiar tubing-bomb methodology, described previously [1]. Thus each candidate (α-hybrid, β-hybrid, and the mixed α- and β-hybrids (denoted α,β-mix) was subjected to thermal stressing in 5% v/v solutions in dodecane (Dod), at both 250 and 425 °C for a period of 1 h under 100-psi initial air pressure. The results are compared visually in Figures 3.1 and 3.2 with those of neat (Dod) as well as 5% v/v solutions containing BzOH and THN. The results are summarized in Table 3.1.

It is immediately evident that the novel THNL-hybrids are not as effective as their original parent structures. There was no apparent synergy. In fact, after 1 h. at 425 °C in Dod these hybrids appear to accentuate degradation, as evidenced by the heavy solid deposits formed and are thus ineffective thermal stabilizers. What is intriguing is that the 50:50 mixture of BzOH/THN appears significantly better as a thermal stabilizer for Dod (and presumably jet fuel) than any of the novel BzOH/THN hybrid molecules.

Originally, for mechanistic purposes, it had been planned to analyze (GC and GC-MS) the thermally stressed mixtures to identify and quantitatively determine the reaction products. However, as the BzOH/THN hybrid molecules performed so poorly as stabilizers in both the autoxidative and pyrolytic regimes, further studies were considered unwarranted.

Table 3.1. Thermal stressing of Dod mixtures containing BzOH/THN hybrids.

Hydrogen Donor: (5% v/v)	Appearance	
	250 °C	425 °C
none (pure Dod)	clear, colorless liquid	clear, yellow liquid + black solid deposits
BzOH	two phases —clear, colorless liquid—clear yellow oil	clear, yellow liquid
THN	clear, very pale yellow liquid	clear, orange liquid
α-hybrid	yellow liquid, evidence of a second phase (gel?)	black/brown suspension— heavy solid deposit
β-hybrid	orange/brown liquid, plus a second phase (gel?)	black/brown liquid + heavy solid deposit
α,β-hybrid	pale yellow liquid, some phase separation + solid deposit	red/brown oily suspension + heavy solid deposit

3.3 Benzyl Alcohol Derivatives

As the initial foray into novel hybrid BzOH-THN stabilizers had not proved as effective as first hoped, attention was focused toward an investigation of simpler benzyl-alcohol derivatives. Many pioneering studies in the field of radical oxidation have shown that the mechanism is susceptible to both steric and electronic influence, and it was hoped to exploit this phenomenon here. Judicious substitution of the aromatic ring with groups of varying electronic character (i.e., inductive versus mesomeric, withdrawing versus donating) should allow interplay, via the molecular orbitals (SOMO), with many of the reactive intermediates involved in both the autoxidative and pyrolytic degradation pathways. Implementation of these subtle changes may significantly affect lifetime and reactivity of the radical species present and thus allow fine-tuning of donor capabilities:
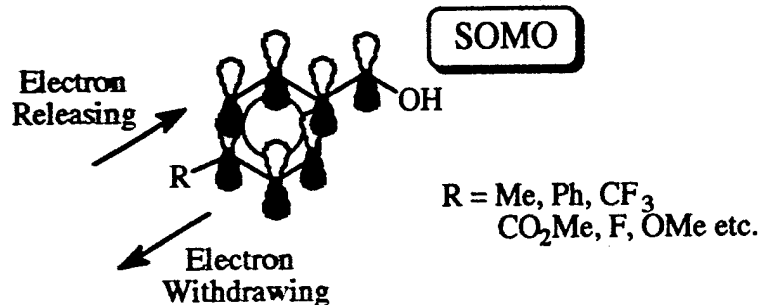
A series of eight *para*-substituted benzylic alcohols was initially chosen for investigation in order to maximize the electronic effect, while keeping any possible steric complications to a minimum. A broad range of varying electronic character was included by first considering the commercially available mono-substituted BzOH's containing the substituents 4-Me-, 4-Ph-, 4-CF$_3$-, 4-MeO$_2$C-, 4-F-, 4-Cl-, 4-MeO-, and 4-PhCH$_2$O-. Past experience has taught us that hydrogen donors containing even relatively short aliphatic side groups (e.g. *n*-butyl, *tert*-butyl, etc.) do not act efficiently as high-temperature thermal stabilizers in jet fuels as they have a tendency to cleave above 400° C and produce radicals that promote degradation. Accordingly, such mono-substituted BzOH's were not considered viable candidates for study. Similarly, other problematic candidate substitutents such as NO$_2$, -CN, etc. were discarded.

It was decided to initially screen the 4-Me-, 4-Ph-, 4-CF$_3$-, 4-MeO$_2$C-, 4-F-, 4-Cl-, 4-MeO-, and 4-PhCH$_2$O- substituted BzOH's for their effectiveness as high-temperature stabilizers in the pyrolytic regime. The rationale being that if a particular substituted BzOH did not exhibit improved (or at least comparable) thermal stabilizing characteristics at 425° C, compared with that of the simple unsubstituted BzOH, it did not warrant further study. This permitted rapid elimination of unfavorable candidates. Thermal stressing of the substituted BzOH's in a molar concentration equivalent to a solution of 5% (v/v) of a Jet A-1 fuel (essentially additive free) was performed in tubing bombs at 425 °C for a period of 1h under 100-psi initial air pressure [1]. For comparison

purposes, the results are compared visually in Figure 3.3 and described, along with those of neat Jet A-1 and a 5% (v/v) BzOH/Jet A-1 solution, in Table 3.2.

Table 3.2. Thermal stressing of Jet A-1 mixtures containing mono-substituted BzOH derivatives.

Hydrogen Donor (5% v/v)	Appearance
none	cloudy yellow liquid—trace of deposit
BzOH	pale yellow liquid—no deposit
4-Me-BzOH	cloudy brown liquid— significant deposit
4-Ph-BzOH	cloudy brown liquid— significant deposit
4-CF$_3$-BzOH	cloudy yellow liquid—no deposit
4-MeO$_2$C-BzOH	dark red liquid—heavy deposit
4-F-	dark red liquid—oily deposit
4-Cl-	black/brown suspension—heavy deposit
4-MeO-	cloudy yellow/orange liquid—no deposit
4-PhCh$_2$O-	dark brown liquid—heavy deposit + tar

Clearly, at 425° C under an initial air pressure of 100 psi, the 4-Me-, 4-Ph-, 4-MeO$_2$C-, 4-F-, 4-Cl-, and 4-PhCH$_2$O- derivatives performed poorly with no obvious correlation with electronic character. While this could have been predicted for the MeO$_2$C- and 4-PhCH$_2$O-BzOH derivatives, because of the relative susceptibility of the substitutents to thermal cleavage, the 4-Me-BzOH and 4-Ph-BzOH results were somewhat surprising. Only the trifluoromethyl and methoxy candidates were deemed worthy of further inquiry, as illustrated visually in Figure 3.4, and the effects of substitution pattern (ortho-, meta-, and para-) and multiplicity (mono-, bis-, and up to penta-) were thus restricted to these two types of substituted hydrogen donors.

Scouting experiments designed to examine possible effects of the substitution pattern and multiple substitution on high-temperature stabilization were performed by thermal stressing (425 °C for 1h under 100-psi initial air pressure) mixtures of the

commercially available BzOH's containing the substituents 2-MeO-, 3-MeO-, 4-MeO-, 2,3-(MeO)$_2$-, 2,4-(MeO)$_2$-, 2,5-(MeO)$_2$-, 3,4-(MeO)$_2$-, 3,5-(MeO)$_2$-, 2,3,4-(MeO)$_3$-, 2,4,5-(MeO)$_3$-, and 3,4,5-(MeO)$_3$-. Again a molar concentration equivalent to a solution of 5% v/v of a Jet A-1 fuel (essentially additive free) was employed. These experiments were performed in a set of new tubing bombs (the old ones needed to be replaced), and the results obtained for the "pure" Jet A-1 fuel (no additives or added hydrogen donors) and that containing 4-MeO-BzOH were not entirely consistent with those given previously in Table 3.2. This illustrates that the composition of the metal tubing bomb and the "aging" process that occurs during repeated use can have a marked effect on the degradation of the jet fuel and the formation of carbonaceous deposits. For the scouting studies, however, it is the comparison between "pure" jet fuel and the mixtures containing the hydrogen donors that is important. Table 3.3 summarizes the results.

Table 3.3. Thermal stressing of Jet A-1 mixtures—
Effect of substitution pattern and multiple substitution.

Hydrogen Donor (5% v/v)	Appearance
none	red brown liquid—minor black deposit
2-methoxy-BzOH	dark brown opaque liquid—black oily film deposit
3-methoxy-BzOH	pale yellow liquid— black deposit (THF soluble)
4-methoxy-BzOH	pale orange liquid—light deposit (THF insoluble)
2,3-dimethoxy-BzOH	clear brown liquid—black oily film
2,4-dimethoxy-BzOH	clear red/brown liquid—black oily film
2,5-dimethoxy-BzOH	clear brown liquid—black oily deposit
3,4-dimethoxy-BzOH	clear red/brown liquid—black oil and solid deposit
3,5-dimethoxy-BzOH	clear yellow liquid—black oily phase
2,3,4-trimethoxy-BzOH	clear brown liquid—heavy black deposit
2,4,5-trimethoxy-BzOH	clear dark brown liquid—heavy black grainy deposit
3,4,5-trimethoxy-BzOH	clear dark brown liquid—very heavy black deposit

The results are at best disappointing, but clearly there are no obvious advantages in pursuing the mono-substituted 2-MeO- and 3-MeO-BzOH derivatives or any of the dimethoxy- and trimethoxy-BzOH's as potential superior stabilizers for jet fuels in the pyrolytic regime. In fact, only the 4-MeO-BzOH exhibited any promise as a high-temperature stabilizer, and even in this case it is not superior to the unsubstituted BzOH. Once again we are reminded of one of the important "rules of thumb" for effective high-temperature hydrogen donors [3,4]: The more uncomplicated the chemical structure (i.e., the absence of side groups) the more efficient the high-temperature thermal stabilizer.

At this point it became evident that the forays into methoxy-modified BzOH's had produced little or no improvement over simple BzOH. Attention was now focussed on the other set of modified BzOH's where there was reason for optimism, the trifluoromethyl substituted-BzOH's. Thermal stressing (425 °C, 1h, under 100-psi initial air pressure) was performed on mixtures of five commercially available trifluoromethyl compounds, 2-CF_3-, 3-CF_3-, 4-CF_3-, 2,5-$(CF_3)_2$-, and 3,5-$(CF_3)_2$-BzOH, in dodecane (Dod) using a molar concentration equivalent (0.483 M) to a solution of 5% (v/v) BzOH (Unfortunately the "additive-free" Jet A-1 sample used in the above experiments was no longer available, and to date we have been unable to obtain an appropriate substitute.) The results, which are summarized in Table 3.4, are more encouraging but still leave room for improvement. The 4-CF_3-BzOH candidate can be singled out, although this choice must take into account expense ($\approx$ $6.76 per gram) and possible toxicity concerns. Indeed, during many of these experiments fumes were observed after thermal stressing, possibly indicating the liberation of HF. This behavior is undesirable for a high-temperature jet fuel.

Table 3.4. Thermal stressing of dodecane mixtures —
Trifluoromethyl-substituted benzyl alcohols.

Hydrogen Donor (5% v/v)	Appearance
none (pure Dod)	clear, yellow liquid + black solid deposits
BzOH	clear yellow liquid
2-CF$_3$-BzOH	clear pale amber liquid — trace of very fine particulate deposit
3- CF$_3$-BzOH	clear pale amber liquid — trace of black oily deposit
4- CF$_3$-BzOH	clear, near colorless liquid — trace of a pale yellow phase evident
2,5-(CF$_3$)$_2$-BzOH	orange/yellow liquid — trace of black oily phase
3,5-(CF$_3$)$_2$-BzOH	orange/yellow liquid — heavy crystalline deposit (additive m.p. 54-56° C)

3.4   Ethyl Acetate

Dr. Tim Edwards of Wright-Patterson AFB drew our attention to some Russian work on pyrolytic stabilizers in which they claimed that ethyl acetate (EAc) was a potential high-temperature stabilizer for jet fuel. Although we were unable to rationalize chemically why this may be so, thermal-stressing experiments were performed using the same tubing-bomb methodology described previously [1]. Mixtures of jet fuel (Jet A-1) or dodecane (Dod) containing 5 % (v/v) ethyl acetate were stressed under 100 psi of air at 425° C for periods of up to 8 h.

The results, qualitatively summarized in Table 3.5, show that EAc is not an effective stabilizer (in terms of suppressing the formation of carbonaceous solids) in the pyrolytic regime (425° C) under the concentrations employed. After 1 h of thermal stressing, there is a significant amount of solids suspended in a pale yellow liquid. After more than 4 h, the liquid is black with suspended solids. Mixtures stressed for 3 or more hours produced a considerable amount of gas (after cooling the pressure is considerably

higher than the original 100 psi), which suggests that severe degradation has taken place. If we compare the results with those obtained previously, we conclude that the Jet A-1/EAc or Dod/EAc mixtures are no more stable at 425°C under an initial pressure of 100-psi air than "pure" Jet A-1 or Dod (in fact they may be slightly worse), and certainly not as good as any of the analogous mixtures containing the hydrogen donors, tetrahydroquinoline (THQ), tetralin (THN), or benzyl alcohol (BzOH).

Table 3.5. Thermal stressing of Jet A-1 and Dod mixtures containing EtAc.

Time: (h)	Appearance	
	Jet A-1 Fuel	Dodecane
1	very pale yellow liquid—suspended solids	very pale yellow liquid—suspended solids
2	yellow liquid—trace of solids	yellow liquid—suspended solids
3	bright yellow liquid—trace of solids	yellow liquid—suspended solids
4	orange/red liquid—trace of solids	dark yellow liquid—suspended solids
6	black liquid—black solids	red/black liquid—suspended solids
8	black liquid—black solids	black liquid—large suspended solids

3.5 Ramifications

Having examined numerous hybrid and functionalized hydrogen donors based upon BzOH and THN, we are forced to conclude that the structural (molecular) simplicity (i.e. the absence of substituents) of THQ, THN, and BzOH and their reaction products are key factors in the design of efficient high-temperature thermal stabilizers for jet fuels and the like in the pyrolytic regime. No derivative was found that was superior to THQ, THN, or BzOH.

Results of thermal stressing in dodecane: @ 250°C - the autoxidation regime

| neat | BzOH | Tetralin | 'α' | 'β' | 'mix' |
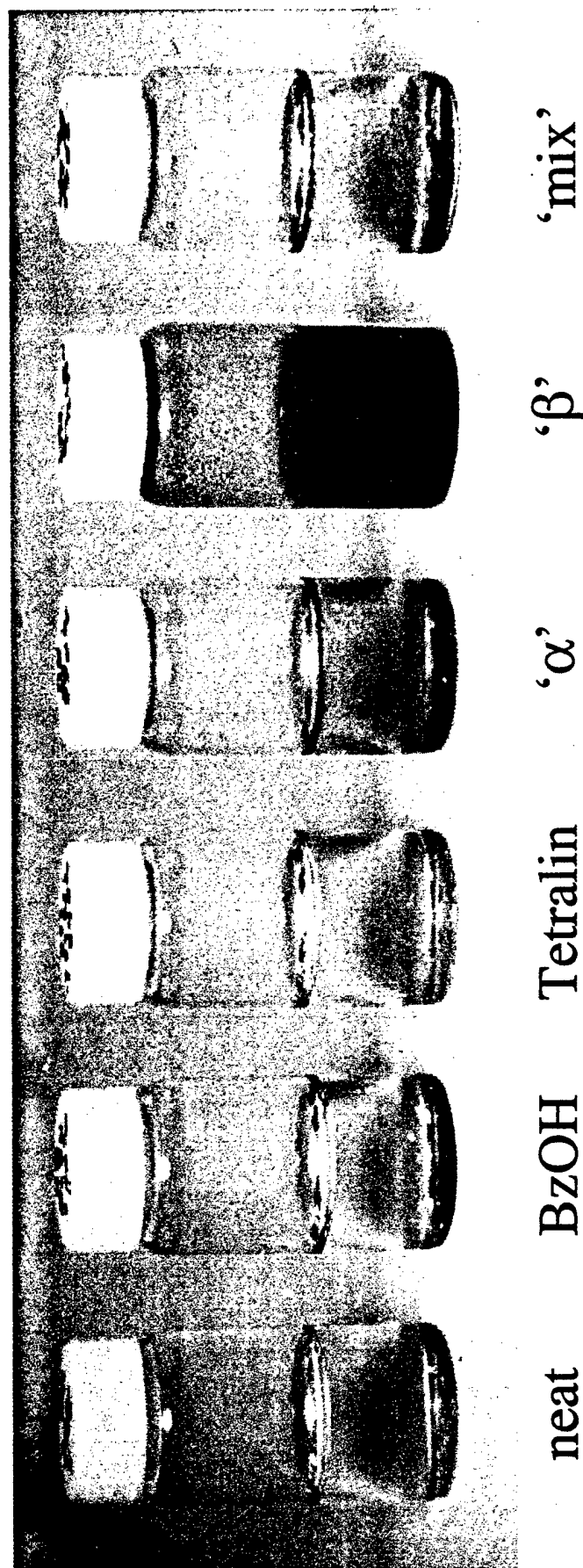
• 5% v/v solutions in dodecane, 100 psi air, 1 h @ 250°C

Fig 3.1

Results of thermal stressing in dodecane: @ 425°C - the pyrolysis regime
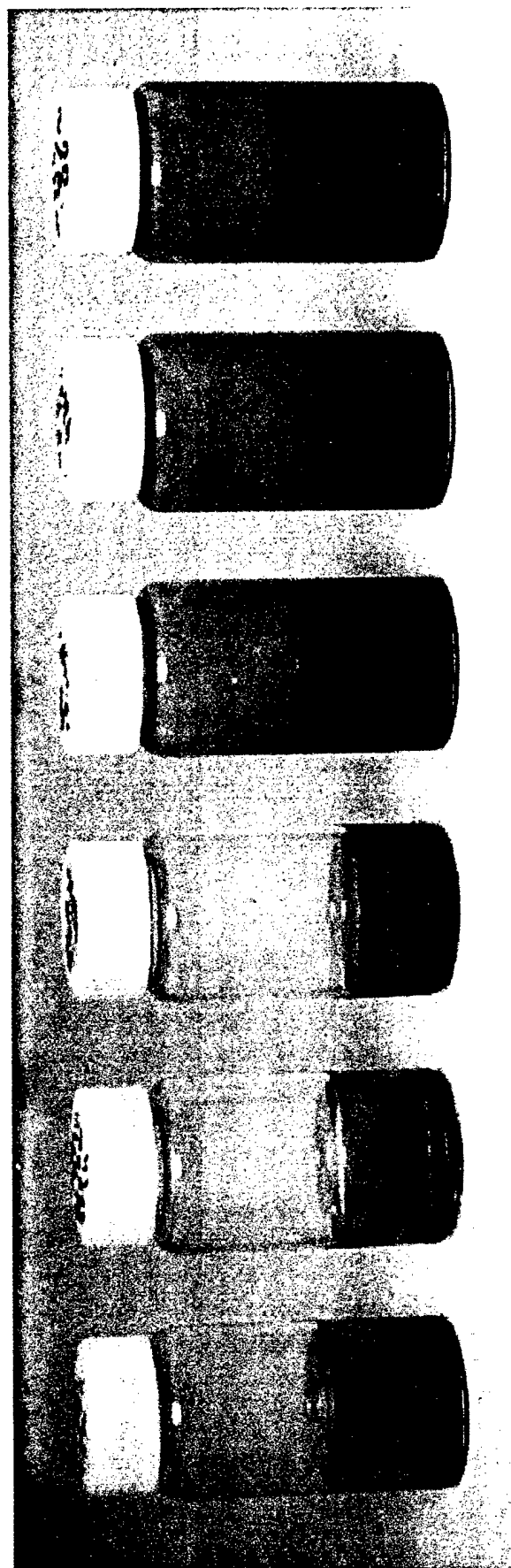
| neat | BzOH | Tetralin | 'α' | 'β' | 'mix' |

• 5% v/v solutions in dodecane, 100 psi air, 1 h @ 425°C

Fig 3.2

Screening of candidates by thermal stressing in Jet Fuel A-1

4-Me- 4-Ph- 4-CF$_3$- 4-MeO$_2$C- 4-F- 4-Cl- 4-MeO- 4-PhCH$_2$O-
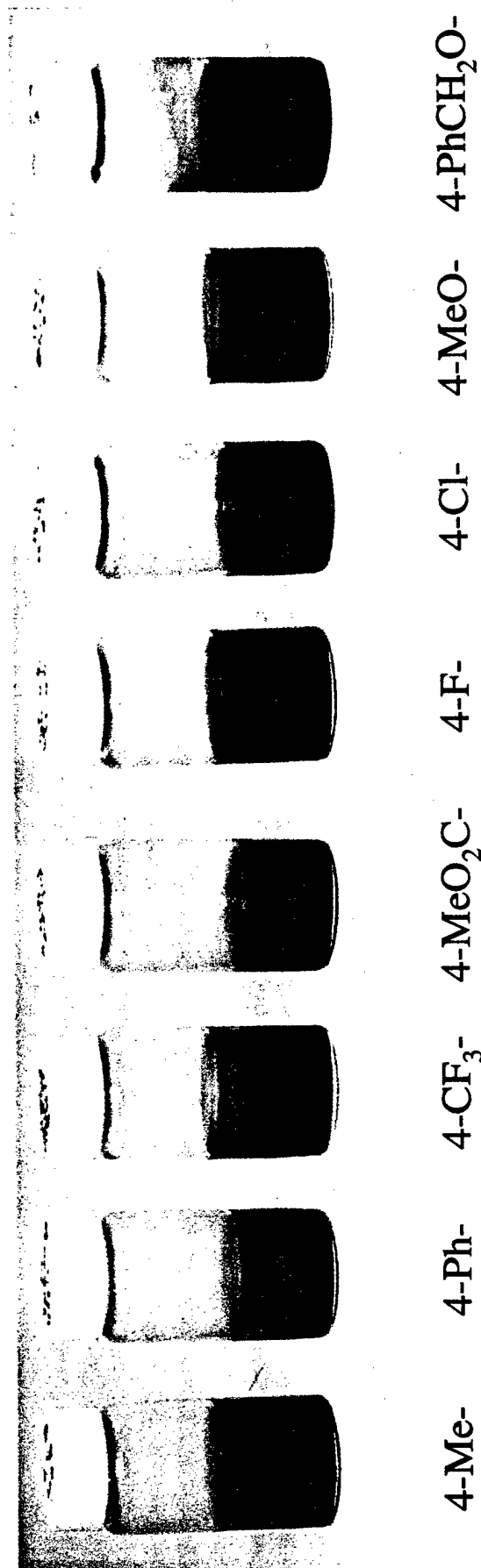
- 'normalized' 5% v/v solutions, 100 psi air, 1 h @ 425°C

Fig 3.3

29

A quick comparison…

neat   BzOH   4-CF$_3$-   4-MeO-
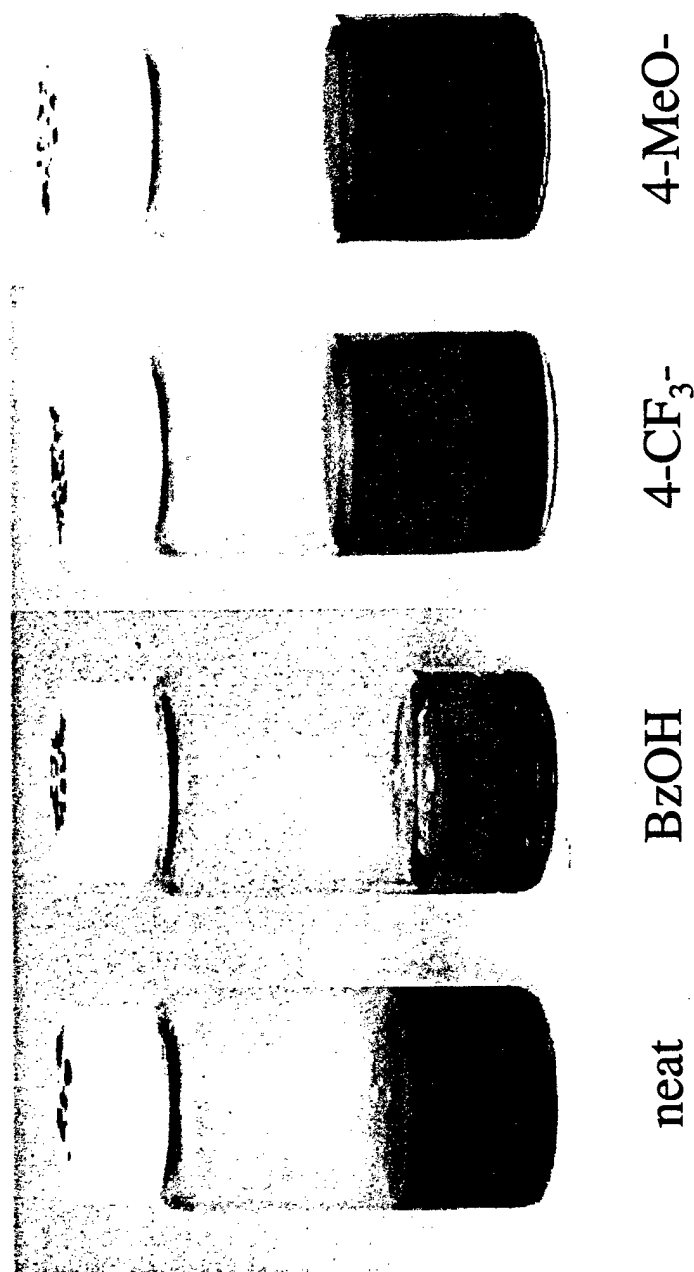
- 'normalized' 5% v/v solutions in Jet Fuel A-1, 100 psi air, 1 h @ 425°C

Fig 3.4

4.0 LOW-TEMPERATURE OXIDATION RESISTANCE OF THERMAL STABILIZERS

4.1 Background

The need and rationale for the development of jet fuels and similar hydrocarbon mixtures with enhanced thermal stability at temperatures above 400 °C (the so-called pyrolytic regime [17]) has been detailed in previous publications [2-4]. Cleavage of carbon-carbon bonds into free radicals is facile at these temperatures and leads to the rapid degradation of aliphatic hydrocarbons with ensuing formation of insoluble carbonaceous materials. Nevertheless, it has been shown that the formation of carbonaceous materials can be significantly retarded in jet fuel mixtures by the addition of hydrogen-donor molecules. In essence, these hydrogen donors "cap" the aliphatic-carbon radicals formed in the pyrolytic regime, while themselves transforming into relatively stable products [3-4]. Kinetic studies reveal that the rate of hydrocarbon degradation in the mixtures is a very strong function of temperature above 400 °C, however, and thus stabilization of hydrocarbon fuels (in terms of the deposition of solids) does not appear practical at temperatures much above 475-500 °C using hydrogen donors [4].

Three of the most effective high-temperature stabilizers for hydrocarbon fuels in the pyrolytic regime found so far are 1,2,3,4-tetrahydroquinoline (THQ), tetralin (THN), and benzyl alcohol (BzOH) [3,4]. The former, THQ, is superior to the others, which is predicated upon a number of factors. First, THQ and its dominant reaction product, quinoline, are highly stable at 400-450 °C—there are no substituents on the aromatic or aliphatic rings which can be cleaved at these temperatures to produce radicals and promote degradation. Secondly, THQ is a highly efficient radical scavenger at these temperatures. Initial hydrogen abstraction by an aliphatic-hydrocarbon radical is facile and the THQ aza-radical formed is well stabilized by resonance through delocalization into the aromatic ring. Finally, the transfer of three more hydrogens to hydrocarbon

radicals is also facile with excellent resonance stabilization at every step toward the formation of quinoline [3,4].

However, having successfully discovered compounds that act as thermal stabilizers for hydrocarbon mixtures at temperatures in the pyrolytic regime, we are now confronted with a number of questions, the answers to which will have important ramifications in the design, formulation, and development of commercially viable high-temperature stable jet fuels. Such fuels must also prove stable (both thermally and oxidatively) at storage and moderately elevated temperatures (from ambient to say 300 °C), and there are some perplexing problems on the horizon. The very chemical and structural characteristics that render THQ (and similar hydrogen donors) effective thermal stabilizers in the pyrolytic regime also accentuate the susceptibility to oxidation in the so-called autoxidation regime between 150 and 300 °C. Elimination of oxygen from the fuel might be a feasible strategy, but not an attractive one. Just how sensitive are THQ, THN, and similar compounds to oxidation in the presence of air at moderate temperatures ($\approx$ 250 °C)? Will they act as benign oxygen scavengers, or will they promote autoxidation at these temperatures and contribute to the formation of gums and insoluble carbonaceous materials? If the latter occurs, can we find other antioxidants (or "sacrifical lambs") that will protect the hydrogen donor from oxidation and at the same time not promote degradation in the pyrolytic regime? This represents a real challenge because classic antioxidants such as the sterically hindered phenolics that operate well in the autoxidation regime actually *promote* free-radical reactions in the pyrolytic regime. In other words, the additive introduced to prevent degradation of the fuel in storage and at moderately elevated temperatures can adversely affect the efficacy of the additive introduced to retard the formation of carbonaceous solids at high temperatures (> 400 °C). In an attempt to answer some of the above questions, a series of simple qualitative thermal-stressing experiments was performed at 250 °C under different atmospheres.

4.2 Susceptibility of Neat Hydrogen Donors to Oxidation

In the first set of experiments, neat THQ, THN, and BzOH were thermally stressed at 250 °C for 1 h under an initial air pressure of 100, 200, 300, and 400 psi. This was followed by an analogous set of experiments performed at an initial pressure of 100 psi air, UHP-nitrogen, or argon for periods of 15, 30, and 60 min. Thermal stressing was performed on 10-mL samples at 250 °C in 25-mL type 316 stainless-steel micro-reactors under different initial pressures of air, UHP-grade N_2, or argon [1-4]. The micro-reactor containing the sample was purged with the gas five times at 1000 psi (6.9 MPa) to minimize the presence of dissolved gases before final pressurization. It was then placed in a preheated sand bath at 250 °C for the required stressing time, followed by quenching into cold water. For the purposes of these "scouting" studies, only visual observations of the products of thermal stressing were made—detailed chemical analysis was not considered necessary.

Figure 4.1 shows a typical example of the results obtained following thermal stressing at 250° C. Even under the mildest of the stressing conditions (10 min at 250 °C under initial 100-psi air), neat THQ transforms into a dark black liquid with a measurable amount of suspended black solids. Increasing the stressing time or the initial pressure of air simply exacerbates degradation to the point (1 h at 400 psi air) where the sample contains a large amount of black suspended solids and obvious deposits on the reactor wall. THN is less susceptible to oxidative degradation under the same stressing conditions, but nonetheless degrades significantly (e.g. under initial 100-psi air, the sample transforms into a brown/black liquid with a trace of solids after 60 min at 250 °C). Under similar conditions, BzOH appears to be only slightly affected (after 1 h under initial 100-psi air, the sample has a very pale yellow appearance, but there are no signs of gum or solid formation). When air is replaced by UHP-nitrogen or argon, the results provide evidence for the crucial role of oxygen. Under these "inert" atmospheres, the THQ sample becomes distinctly colored. Similarly, both the THN and BzOH samples

exhibit a slight coloration upon stressing. In all cases, however, there was no evidence of the formation of gums or solid carbonaceous materials. From these simple experiments, we conclude that BzOH is significantly less susceptible to reaction with oxygen at 250 °C than is THN, which in turn, is significantly less susceptible than is THQ.

4.3 Classic Antioxidants

Classic antioxidants such as sterically hindered phenolics are known to operate well in the autoxidation regime. Does the addition of 200 ppm of an antioxidant such as 2,6-di-*tert*-butyl-*p*-hydroxytoluene (BHT) improve the oxidative stability of the hydrogen donors at 250 °C? The answer apparently is no. In another set of experiments, neat THQ, THN, and BzOH were stressed in the presence of 200-ppm BHT at 250 °C for 1 h under an initial pressure of 100 psi of air. Little or no difference was observed.

4.4 Mechanistic Considerations

It might be expected that THQ, and to a lesser extent THN, are both highly susceptible to oxidation in the autoxidative regime. Consider Scheme 4.1 where THN is used to illustrate the major reactions that are most likely to occur in the autoxidative and pyrolytic regimes in the presence of oxygen. THN has four hydrogens adjacent to the phenyl ring that are particularly susceptible to abstraction by an alkyl radical. The resultant radical (I) is well stabilized by resonance throughout the aromatic ring. At the high temperatures of the pyrolytic regime (> 400 °C), even in the presence of small concentrations of oxygen, abstraction of a second hydrogen by an alkyl radical is the more facile reaction, leading to (II). The allylic hydrogens adjacent to the double bond become activated, which leads to the sequential abstraction of two additional hydrogens and finally to the relatively stable end product, naphthalene (III). This ability to transfer hydrogens and "cap" alkyl radicals in the early stages of their formation is responsible for THN and THQ being excellent stabilizers for hydrocarbon fuels in the pyrolytic regime [18].

The situation at 250 °C in the presence of oxygen, however, is very different. Here the classic autoxidation mechanism becomes the dominant reaction path. After abstraction of the initial hydrogen (I), rather than further abstraction of the adjacent hydrogen by an alkyl radical (II), molecular oxygen is inserted producing the peroxy radical (IV). This is followed by the classic steps of formation of a hydroperoxide (V) and decomposition of the hydroperoxide to form two oxy radicals (VI), which, in turn, can undergo a variety of reactions (including radical addition, cleavage, and rearrangement) yielding a large number of possible oxidation products. It is the proliferation of propagative pathways by this self-initiating process that is the hallmark of autoxidative degradation.
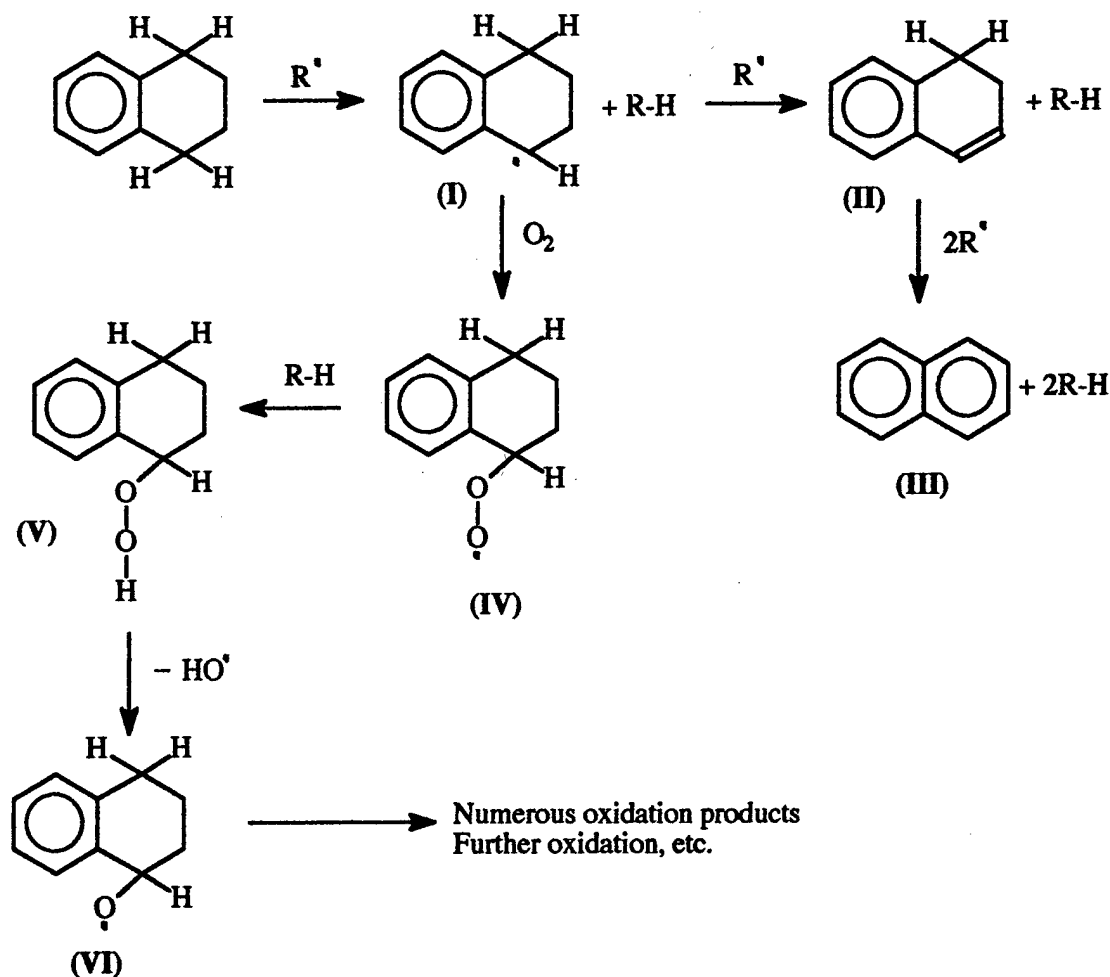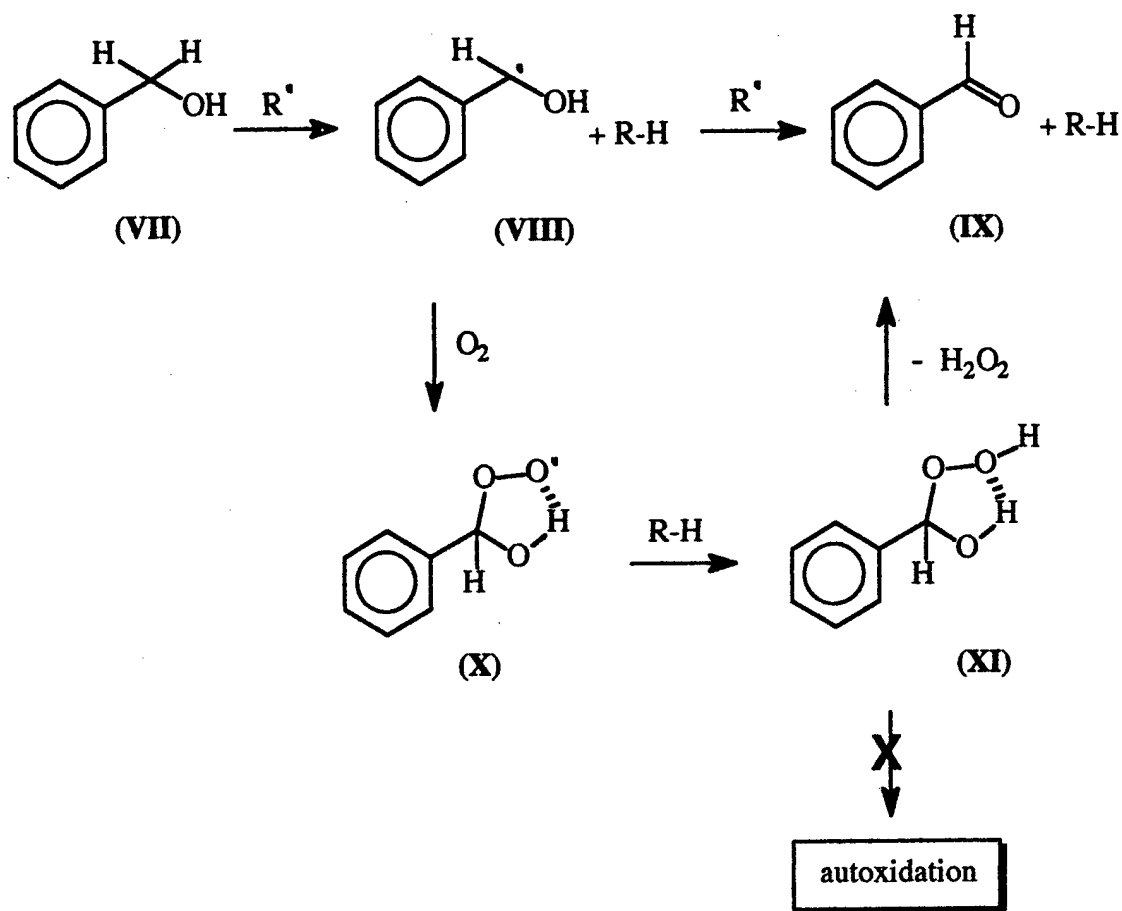

Scheme 4.1

To reiterate, the very chemical and structural characteristics that make THN, THQ, and similar hydrogen donors effective thermal stabilizers in the pyrolytic regime also renders them highly susceptible to oxidation in the autoxidation regime. Moreover, the addition of phenolic antioxidants does not appear to improve matters, judging from the limited studies we have performed. This will not be a trivial problem if we intend to employ THQ or THN as a high-temperature stabilizer in jet fuels. Possible solutions to this dilemma, which in themselves pose numerous other questions, include the total elimination of oxygen in the fuel or the selective addition of THQ (or THN) *in situ* immediately prior to the fuel's reaching a temperature > 400 °C.

There is one bright spot on the horizon, however. BzOH, the first high-temperature stabilizer we discovered [1], while not as efficient as THQ at temperatures in the range of 400-500 °C [3,4], is not normally considered a classic hydrogen donor. The mechanism of oxidation at 250 °C appears to be different from that of THQ and THN, and this warrants further investigation. Thus far we have identified three possible reasons for this difference, which are summarized in Scheme 4.2.

(1)   Initial abstraction of a hydrogen atom from BzOH (i.e. **VII** to **VIII**) is slower than in the analogous case of THN. Although no direct comparisons have been made, certainly this step has been shown to be susceptible to both steric [19] and electronic factors [20].

(2)   Intermediates such as the peroxy radical (**X**) and the hydroperoxide radical (**XI**) are stabilized by hydrogen bonding. Both inter- [21] and intramolecular [22] hydrogen bonds have been shown to greatly reduce the rate of ensuing propagative steps.

(3)   A competing decomposition prevails. Indeed BzOH itself undergoes an alternative breakdown pathway to benzaldehyde (**IX**) and hydrogen peroxide, unlike other similar α-substituted toluenes [23].

Scheme 4.2

Although at this stage it is not possible to state which of these mechanisms is instrumental, all may appear plausible conspirators in preventing the expected autoxidation cascade. As in the pyrolytic regime, donation of an additional hydrogen results in a formal oxidation to benzaldehyde [1,2].

4.5 "Unhindered" Phenols

Hindered phenols such as 2,6-di-t-butyl-4-hydroxytoluene (BHT) are effective antioxidants for jet fuels in the autoxidative regime, but unfortunately accentuate degradation in the pyrolytic regime because the t-butyl side groups cleave at these high temperatures and are an additional source of free radicals. While sterically hindered
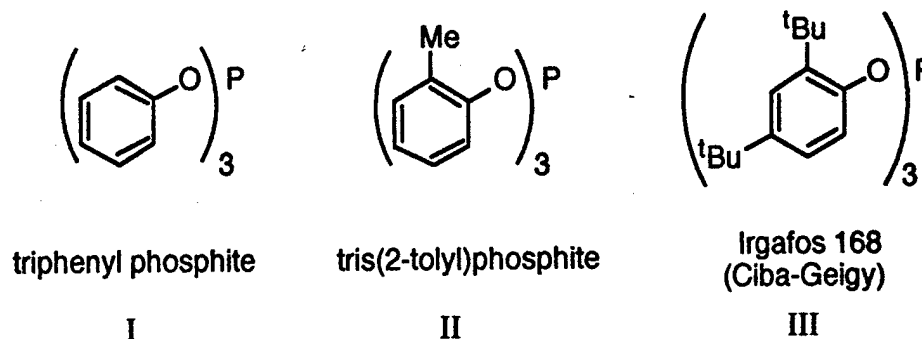
37

phenolic molecules in the 2 and 6 positions have been found to be the most effective antioxidants at relatively low temperatures, other phenolic molecules have shown at least some antioxidative activity, and it was surmised that phenolic molecules without "cleavable" side groups might protect both the jet fuel and the high-temperature stabilizers [i.e. BzOH, THN, THQ, etc.] as the fuel passes through the autoxidative temperature regime.

Initial results from scouting experiments demonstrated that Dod mixtures containing 200 ppm of phenol (PhOH) or 2,6-dimethylphenol (DMPh) remained clear (albeit slightly colored) liquids with no evidence of phase separation or solid formation for periods of up to at least 4 h at 250 °C under an initial pressure of 100-psi air. This was an improvement over the results obtained for neat Dod (which shows evidence of phase separation after 3 h of thermal stressing at 250°C). The important question was: Does the addition of PhOH to the Dod mixture containing BzOH, THN, or THQ protect both the hydrocarbon fuel and the high-temperature stabilizer while the mixture passes through the autoxidative regime? The answer appears to be no. Mixtures of Dod containing 5% THQ and varying amounts of PhOH, ranging from 200 ppm to 1%, became highly colored with an obvious phase separation after 1 h at 250 °C under 100-psi air. Evidently THQ is preferentially oxidized; PhOH is not an effective antioxidant for THQ. The effect of PhOH in the analogous THN and BzOH mixtures is less obvious, but follows a similar trend.

4.6 Aromatic Phosphites

As the classic sterically hindered phenolic antioxidants do not appear to protect the hydrogen donor from oxidation in the autoxidation regime and, moreover, promote degradation in the pyrolytic regime, we decided to abandon this direction and focus our attention on trivalent-phosphorus compounds as potential oxygen scavengers. Such compounds have found wide application as melt stabilizers for polymeric materials during processing. For example, simple aromatic phosphites can function as

hydroperoxide decomposers as well as chain breakers, and a wide variety are commercially available. In initial screening studies the three candidates shown below were selected:

triphenyl phosphite   tris(2-tolyl)phosphite   Irgafos 168
                                                     (Ciba-Geigy)

I   II   III

Preliminary investigations of these three phosphites were carried out using the tubing-bomb methodology described previously [1]. Each candidate was subjected to thermal stressing as a solution in Dod at 425 °C for a period of 1 h under 100-psi initial air pressure, at concentrations in the range of 200-5000 ppm. It was found that Irgafos 168 [tris(2,4-di-*tert*-butylphenyl)phosphite—III] gave a marginally superior performance (possibly due to enhanced solubility in Dod resulting from the presence of the *t*-butyl side groups). The results are described in Table 4.1.

Table 4.1. Thermal stressing of Dod mixtures
containing Irgafos 168.

Irgafos 168	Appearance
none (pure Dod)	yellow liquid + trace of black deposit
200 ppm	very light yellow liquid—trace of suspended solids
500 ppm	yellow liquid—some oily phase no solid deposit
5000 ppm	yellow liquid—black deposit

It was concluded that the addition of 200-500 ppm Irgafos 168 did not appear to accentuate the degradation of Dod in the pyrolytic regime, and these initial results

appeared promising. However, the fact that Irgafos 168 contains two *t*-butyl groups was of some concern. As mentioned above, hindered phenols such as 2,6-di–tert-butyl-4-hydrotoluene (BHT) proved to be effective antioxidants for jet fuel in the autoxidative regime, but actually accentuated degradation in the pyrolytic regime. This was caused by the facile cleavage of these *t*-butyl groups, thus producing additional radicals. Hence key issues that need to be addressed are: "How long will Dod containing 500-ppm Irgafos remain free of carbonaceous solids at 425 °C?" and "How effective is Irgafos 168 as an antioxidant at 250 °C?" To answer these questions, a series of experiments was performed at both 250 °C and 425 °C using the now-familiar tubing-bomb methodology. An initial air pressure of 100 psi was applied and the stressing time was varied from 1 to 6 h. The results are summarized in Table 4.2.

Table 4.2. Thermal stressing of Dod/Irgafos 168 (500 ppm) mixtures.

Time: (h)	Appearance	
	250° C	425° C
1	colorless liquid—no solid deposit	pale yellow liquid—no solid deposit
2	colorless liquid—no solid deposit	pale yellow liquid—no solid deposit
3	very pale yellow liquid— no solid deposit	yellow liquid— trace solids
4	pale yellow liquid— no solid deposit	red/orange liquid— fine suspended solids
5	yellow liquid— no solid deposit	brown/red liquid— suspended solids
6	yellow liquid—some oily phase trace of solids	brown liquid— suspended solids

As can be seen from Table 4.2, the addition of 500-ppm Irgafos 168 to Dod prevents the obvious formation of solids and gums for up to ≈ 5 h at 250 °C. However, at 425° C, carbonaceous solids are detected at times > 2 h. It is believed that cleavage of the *t*-butyl groups limits the effectiveness of Irgafos 168. Accordingly, we turned our

attention to alternative organophosphorous compounds that do not contain long or bulky aliphatic side groups, such as simple aromatic phosphines.

4.7 Aromatic Phosphines

Organophosphines, like most trivalent phosphorous compounds, are very reactive substances. All phosphines are subject to facile oxidation. The simple mono- and dialkyl phosphines have a great affinity for atmospheric oxygen, but aryl phosphines are more stable in this respect. It is also important that the reaction between the scavenger molecule and oxygen not generate free radicals, which could, in turn, initiate fuel oxidation. In essence, our search is for additives that protect both the fuel and the hydrogen donor in the autoxidative regime, yet do not promote free-radical reactions at pyrolytic temperatures. Such additives must be structurally simple and not contain any long side-group substituents that can cleave and produce free radicals above 400° C. With these considerations, we selected triphenylphosphine (TPP) as the initial candidate scavenger for screening. Preliminary studies of TPP were performed using the tubing-bomb methodology previously described. Mixtures of 10-mL Dod and 100-, 200-, and 500-ppm TPP were thermally stressed at 425 °C for a period of 1 h under 100-psi initial air pressure. Results are summarized in Table 4.3.

Table 4.3. Thermal stressing of Dod mixtures containing TPP.

TPP conc.	Appearance
none (pure Dod)	yellow liquid—suspended solids
100 ppm	yellow liquid—trace of suspended solids
200 ppm	yellow liquid—no solids
500 ppm	yellow liquid—no solids

Most importantly, the addition of 200- to 500-ppm TPP does not appear to accentuate the degradation of Dod in the pyrolytic regime. In fact, the mixtures

containing 200- and 500-ppm TPP were, if anything, superior to neat Dod or to the mixture containing 100-ppm TPP. This was an encouraging result.

Additional experiments were performed on neat Dod (for baseline comparison) and Dod mixtures containing 200-ppm TPP for periods of 1, 2, 3, 4, 6, and 8 h at 425°C, under an initial pressure of 100-ppm oxygen. The results indicated that the presence of 200-ppm TPP did not materially affect the time at which solid carbonaceous materials were detected. In other words, solid deposits were observed at times ≥ 3 h, regardless of whether or not 200-ppm TPP was present. This is not unexpected as TPP is a simple molecule, which does not contain side groups and is not a hydrogen donor (which could enhance stabilization at this temperature).

The next set of scouting experiments was designed to see whether TPP is an effective oxygen scavenger at 250° C in the autoxidative regime. Dod mixtures with 100-, 200-, and 500-ppm TPP were thermally stressed at 250° C for a period of 1 h under 100-psi initial air pressure. The addition of 100- or 200-ppm TPP to neat Dod produced liquid products that were visually similar to those obtained from neat dodecane. This does not prove that TPP is an effective oxygen scavenger at 250 °C, but at least the additive did not accentuate oxidative degradation. At 500 ppm, one observes two distinct phases (a minor amount of a yellow oily phase—most likely a solubility problem that should not occur in jet fuel). Additional thermal-stressing studies of Dod mixtures containing 200-ppm TPP at 250 °C under an initial pressure of 100-psi air were performed for periods of 1, 2, 3, 4, 6, 12, 24, 36, and 48 h. These experiments did not produce definitive results. Neither pure dodecane nor the mixtures containing TPP showed any evidence of significant degradation (i.e. gum or carbonaceous deposits). In retrospect, these results are what we might have anticipated, and the only useful piece of information to be gained is that the presence of TPP does not appear to have accentuated degradation at 250° C.

The next stage was to undertake thermal-stressing studies of ternary systems containing Dod/TPP with the hydrogen donors THN, THQ, and BzOH at 250 and 425° C. Dod mixtures containing 5% THQ, with and without TPP (at levels of 100 and 200 ppm), were stressed at 250°C under an initial pressure of 100-psi air for periods of 1, 2, 3, and 4 h. The results were not encouraging. After 1 h, the Dod/THQ mixtures, both with and without TPP, resembled relatively clear supernatant liquors containing reddish-brown deposits. In essence, TPP did not protect the THQ from oxidation at 250°C, and undesirable degradation products were present. In other words, it is apparent that THQ is more readily oxidized than TPP! After 1 h at 425 °C, the Dod/THQ/TPP mixtures may be described as dark-brown liquids with large amounts of black deposits. This is definitely unsatisfactory.

Similar experiments on the analogous Dod/THN/TPP ternary mixtures were performed. In contrast to the THQ systems, both the binary Dod/THN and ternary Dod/THN/TPP (200 ppm) mixtures remained lightly colored liquids after thermal stressing at 250°C for periods of up to 24 h. No evidence of carbonaceous deposits was detected. This suggests that THN is far less susceptible to autoxidation (in terms of measurable deposits) at 250° C as compared with THQ. It remains an open question whether or not the presence of TPP makes any difference in the stability of Dod/THN mixtures at this temperature. On the other hand, at 425° C under an initial air pressure of 100 psi, a trace of carbonaceous solids was noticed after 1 h in the binary Dod/THN mixture. Somewhat more was seen in the ternary Dod/THN/TPP mixture. Degradation became progressively worse with time, and at 3 h, a substantial black deposit was noted in both the binary and ternary mixtures.

BzOH is considered the least susceptible to autoxidation of the three hydrogen donors examined. After thermal stressing at 250° C under an initial air pressure of 100 psi, Dod/BzOH and Dod/BzOH/TPP (200 ppm) mixtures exist in two liquid phases at room temperature. (It should be emphasized that in jet fuels we observe only a single

phase in mixtures with BzOH.) The major phase remains essentially a colorless liquid as a function of time up to about 12 h, while the minor heavy phase becomes progressively colored, but there are no signs of solid carbonaceous materials. Somewhere between 12 and 24 h both the Dod/BzOH and Dod/BzOH/TPP (200 ppm) mixtures become black liquids with heavy deposits. There appears to be little difference between the Dod/BzOH mixtures, with or without TPP. At 425° C, two-phase liquids are observed after thermally stressing the Dod/BzOH/TPP (200 ppm) mixtures up to 2 h. The minor heavy phase is highly colored but does not appear to contain carbonaceous solids. After 2 to 3 h, the mixture transforms into a black liquid with black deposits. This is not encouraging, as it was previously reported that Dod/BzOH mixtures stressed at 425° C under an initial air pressure of 100 psi remained free of carbonaceous solids for at least 6 h [1,2].

4.8 Ramifications

Potential problems arising from the oxidative susceptibility of hydrogen donating, high-temperature stabilizers have not been resolved. THQ, in particular, appears highly vulnerable to oxidative degradation, and we have not been successful in finding suitable additives (antioxidants) that act as "sacrificial lambs", preferentially oxidizing and thus protecting the high-temperature stabilizer. THN and BzOH are less susceptible to autoxidation, and it is our opinion that further work should be focused on these two hydrogen donors, even though they are less efficient as high-temperature stabilizers in the pyrolytic regime. Phosphines and similar compounds, which act as oxygen scavengers, warrant further investigation. To this end, we have approached Professor Bruce Beaver of Dusquene University, an expert in the field, and intend to collaborate with him in the near future.

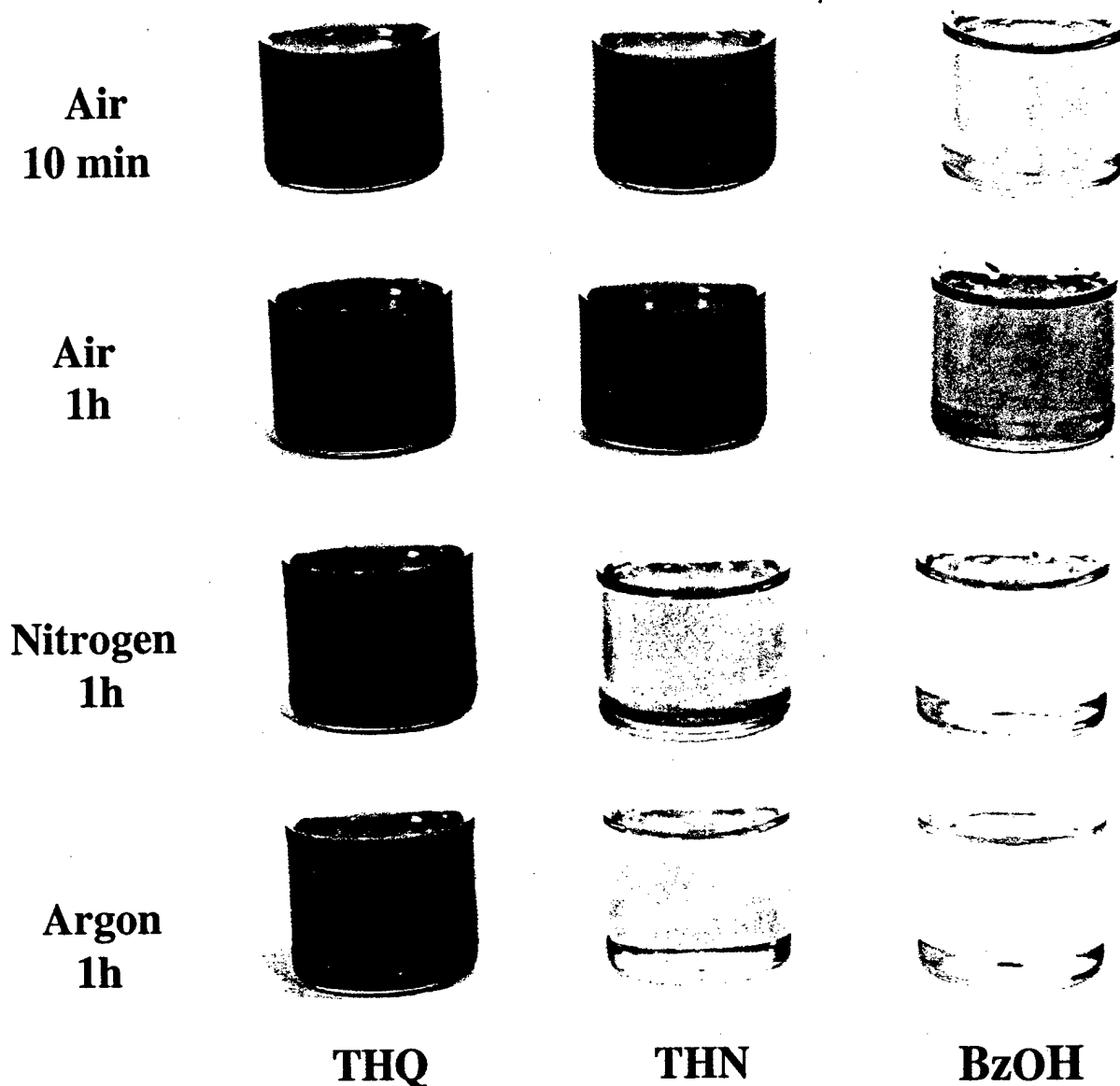# Results of thermal stressing neat THQ, THN and BzOH @ 250°C under different atmospheres

Air 10 min

Air 1h

Nitrogen 1h

Argon 1h

THQ　　　THN　　　BzOH

Fig 4.1

5.0 REFERENCES

1. Coleman, M. M., Selvaraj, L., Sobkowiak, M., Yoon, E., *Energy & Fuels*, **6**, 535 (1992).

2. Selvaraj, L., Sobkowiak, M., Song, C., Stallman, J. B., Coleman, M. M., *Energy & Fuels*, **8**, 839 (1994).

3. Yoon, E. M., Selvaraj, L., Song, C., Stallman, J. B., Coleman, M. M., *Energy & Fuels*, **10**, 806 (1996).

4. Yoon, E. M., Selvaraj, L., Eser, S., Coleman, M. M., *Energy & Fuels*, **10**, 812 (1996).

5. Performed in conjunction with Professor A. Boehman and P. Goel.

6. Song, C., Lai, W-C, Schobert, H. H., *Ind. Chem. Chem. Res.*, **33**, 534, (1994).

7. Kondratiev, V. N., in *Comprehensive Chemical Kinetics*, Vol. 2., Bamford, C. H., Tipper, C. F. H., Eds., Elsevier, Amsterdam (1969).

8. Veytsman, B., Coleman, M. M., *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, **43**, 387-389 (1998).

9. Fearnley, S. P., Sobkowiak, M., Coleman, M. M., *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, **43**, 357-359 (1998).

10. Structure search of the Beilstein database.

11. Monte, A. P., Marona-Lewicka, D., Cozzi, N. V., Nichols, D. E., *J. Med. Chem.*, **36**, 3700 (1993).

12. Adapted from: Jensen, E. H., Nielsen, P. H., Hohlweg, R., *Heterocycles*, **41**, 2441 (1995).

13. Ranu, B. C., Sarkar, D. C., Chakraborty, R., *Synth. Commun.*, **22**, 1095 (1992).

14. Hanack, M., Rieth, R., *Chem. Ber.*, **120**, 1659 (1987).

15. Hanack, M., *Chem. Ber.*, **117**, 3004 (1984).

16. Dolle, R. E., Schmidt, S. J., Kruse, L. I., *J. Chem. Soc., Chem. Commun.*, 904 (1987).

17. (a) Hazlett, R. N., Hall, M., Matson, M., *Ind. Eng. Chem. Prod. Res. Dev.*, **16**, 171 (1977). (b) Hazlett, R. N., In Frontiers of Free Radical Chemistry. Pryor, W. A., Ed., Academic Press, 195 (1980).

18. Coleman, M. M., Sobkowiak, M., Fearnley, S. P., Song, C. *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, **43**, 353-356 (1998).

19. (a) Howard, J. A., Ingold, K. U., Can. J. Chem., **41**, 2800 (1963).

    (b) Howard, J. A., Ingold, K. U., Symonds, M., Can. J. Chem., **46**, 1017 (1968).

    (c) Korcek, S, Chenier, J. H. B., Howard, J. A., Ingold, K. U., Can. J. Chem., **50**, 2285 (1972).

20. Russell, G. A., J. Am. Chem. Soc., **78**, 1047 (1956).

21. Howard, J. A., Schwalm, W. J., Ingold, K. U., Advan. Chem. Ser., **75**, 6 (1968).

22. Rust, F. F., Youngman, E. A., J. Org. Chem., **27**, 3378 (1962).
23. Howard, J. A., Korcek, S., Can. J. Chem., **48**, 2165 (1970).